

→ Radial Equations

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + V_{\text{eff}}^{(l)}(r) \right] R_{nl}(r) = E R_{nl}(r)$$

* Are "n" and "l" enough for $R(r)$?

i) l : obvious $\leftarrow V_{\text{eff}}^{(l)}$

ii) n : "Sturm-Liouville" theory: bound states are non-deg. and Real.
(See also HW#5.1) in 1D.

Thus, $\langle \vec{x} | n, l, m \rangle \equiv \underbrace{R_{nl}(r)}_{\substack{\uparrow \\ \text{radial eg.}}} \underbrace{Y_l^m(\theta, \phi)}_{\substack{\uparrow \\ \text{eigenfunction of } \vec{L}^2 \text{ and } L_z.}}$

④ Spherical Harmonics: $Y_l^m(\theta, \phi) = \langle \hat{n} | l, m \rangle$

$$L_z |l, m\rangle = m\hbar |l, m\rangle \quad \dots (*)$$

$$\vec{L}^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle \quad \dots (**)$$

$$\hat{n} = \frac{\vec{x}}{|\vec{x}|}$$

i)

$$\langle \hat{n} | \cdot (*) : -i\hbar \frac{\partial}{\partial \phi} Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi)$$

$$\rightarrow Y_l^m(\theta, \phi) \propto \exp[i m \phi]$$

: Integer m's are only allowed!

Here, we're talking about "spatial" wave functions.

→ $\psi(r, \theta, 0) = \psi(r, \theta, 2\pi)$ to be single-valued
in space ^{position}.

☆☆☆

$m = \text{integers} : -l, -l+1, \dots, l-1, l.$

so, \hookrightarrow

$l = \text{integers.}$

☆☆☆

for the "orbital"
angular momentum.

ii) $\langle \hat{n} | \cdot (**) :$

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$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + l(l+1) \right] Y_l^m(\theta, \phi) = 0$$

• Approach 1: You can just solve the diff. eq.

$$\hookrightarrow \left[\left(\sin \theta \frac{\partial}{\partial \theta} \right)^2 + \frac{\partial^2}{\partial \phi^2} \right] Y_l^m(\theta, \phi) = -l(l+1) \sin^2 \theta Y_l^m(\theta, \phi)$$

: θ and ϕ are separable, $Y_l^m(\theta, \phi) = e^{im\phi} \cdot f_l^m(\theta)$

and by setting $x \equiv \cos \theta$, $f_l^m(\theta) \rightarrow P_l^m(\cos \theta)$

$$\hookrightarrow \frac{d}{dx} \left[(1-x^2) \frac{dP_l^m}{dx} \right] + \left[l(l+1) - \frac{m^2}{1-x^2} \right] P_l^m(x) = 0$$

$\hookrightarrow P_l^m(x)$: the associated Legendre function.

$$\Rightarrow Y_l^m(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} (-1)^m e^{im\phi} P_l^m(\cos \theta) \quad \text{for } m \geq 0$$

for $m < 0$, use $Y_l^{-m}(\theta, \phi) = (-1)^m \left[Y_l^m(\theta, \phi) \right]^*$
 \uparrow
 a property of P_l^m .

Normalization:

$$\int d\Omega Y_{l'}^{m'} Y_l^m = \delta_{l'l'} \delta_{m'm} \quad \parallel \quad \int d\Omega = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta$$

\uparrow
Solid angle

Associated Legendre function:

$$P_l^m(x) = (-1)^m (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_l(x) \quad \parallel \quad m \geq 0$$

\uparrow

\hookrightarrow Legendre polynomial.

Approach 2 : compute $\langle \hat{n} | l, l \rangle$; lower with L_- .

$$L_+ |l, l\rangle = 0 : -i\hbar e^{i\phi} \left[r \frac{\partial}{\partial \theta} - i r \cot \theta \frac{\partial}{\partial \phi} \right] Y_l^l(\theta, \phi) = 0$$

$$\Rightarrow Y_l^l(\theta, \phi) = C_l e^{i l \phi} \sin^l \theta$$

use the normalization to determine C_l .

$$\Rightarrow |C_l|^2 \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta) \sin^{2l} \theta = 1$$

$$\begin{aligned} \hookrightarrow \int_{-1}^1 dx (1-x^2)^l &= \frac{x}{1} (1-x^2)^l \Big|_{-1}^1 - \int_{-1}^1 dx x \cdot l \cdot (1-x^2)^{l-1} \cdot (-2x) \\ &\quad \text{(int. by parts)} \\ &= \frac{x}{1} (1-x^2)^l \Big|_{-1}^1 - \int_{-1}^1 dx \frac{2}{3} x^3 (1-x^2)^{l-1} \\ &= l \cdot \frac{2}{3} x^3 (1-x^2)^{l-1} \Big|_{-1}^1 - \int_{-1}^1 dx \frac{2}{3} x^3 l(l-1) (1-x^2)^{l-2} \cdot (-2x) \\ &= l \cdot (l-1) \frac{2 \cdot 2}{1 \cdot 3 \cdot 5} x^5 (1-x^2)^{l-2} \Big|_{-1}^1 - \int_{-1}^1 \dots \\ &\vdots \\ &= l! \cdot \frac{2^l}{(2l+1)!!} \cdot 2 = \frac{(2^l l!)^2}{(2l+1)!} \cdot 2 \end{aligned}$$

$$\Rightarrow |C_l|^2 \cdot \frac{(2^l l!)^2}{(2l+1)!} \cdot 4\pi = 1$$

$$C_l = e^{i\alpha} \cdot \frac{1}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}}$$

choose $e^{i\alpha} = \underline{(-1)^l}$: To obtain Y_l^0 with the same sign as $P_l(\cos \theta)$.

$$\Rightarrow C_l = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}}$$

↑ It's convention.

$$\Rightarrow Y_l^l(\theta, \phi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} e^{il\phi} \sin^l \theta$$

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To lower m , use $L_- |l, m\rangle = \sqrt{(l+m)(l-m+1)} \hbar |l, m-1\rangle$

Step 1.

$$\left(\frac{L_-}{\hbar}\right) |l, l\rangle = \sqrt{2l \cdot 1} |l, l-1\rangle$$

$$\left(\frac{L_-}{\hbar}\right)^2 |l, l\rangle = \sqrt{2l \cdot 1} \left(\frac{L_-}{\hbar}\right) |l, l-1\rangle = \sqrt{2l \cdot (2l-1) \cdot 1 \cdot 2} |l, l-2\rangle$$

\vdots

$$\begin{aligned} \left(\frac{L_-}{\hbar}\right)^{l-m} |l, l\rangle &= \sqrt{2l \cdot (2l-1) \cdots (l+m+1) \cdot 1 \cdot 2 \cdots (l-m)} |l, m\rangle \\ &= \sqrt{\frac{2l! (l-m)!}{(l+m)!}} |l, m\rangle \end{aligned}$$

$$\Rightarrow Y_l^m(\theta, \phi) = \sqrt{\frac{(l+m)!}{2l! (l-m)!}} \left(\frac{L_-}{\hbar}\right)^{l-m} |l, l\rangle$$

Step 2

$$\left(\frac{L_-}{\hbar}\right) Y_l^l = + e^{-i\phi} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi}\right) Y_l^l$$

$$= -c_l e^{i(l-1)\phi} \left(\frac{\partial}{\partial \theta} + l \cot \theta\right) \sin^l \theta$$

$$= -c_l e^{i(l-1)\phi} \cdot \frac{1}{\sin^l \theta} \frac{\partial}{\partial \theta} (\sin^l \theta \cdot \sin^l \theta) \quad \left\| \frac{\partial}{\partial \cos \theta} = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right.$$

$$= c_l e^{i(l-1)\phi} \cdot \frac{1}{\sin^{l-1} \theta} \frac{\partial}{\partial \cos \theta} \sin^{2l} \theta$$

$$\left(\frac{L_-}{\hbar}\right)^2 Y_l^l = -c_l e^{i(l-2)\phi} \left(\frac{\partial}{\partial \theta} + (l-1) \cot \theta\right) \left(\frac{1}{\sin^{l-1} \theta} \frac{\partial}{\partial \cos \theta} \sin^{2l} \theta\right)$$

$$= -c_l e^{i(l-2)\phi} \frac{1}{\sin^{l-2} \theta} \frac{\partial}{\partial \theta} \left(\sin^{l-1} \theta \cdot \left(\downarrow \right) \right)$$

$$= c_l e^{i(l-2)\phi} \frac{1}{\sin^{l-2} \theta} \left(\frac{\partial}{\partial \cos \theta}\right)^2 \sin^{2l} \theta$$

\vdots

$$\Rightarrow \left(\frac{L_-}{\hbar}\right)^{l-m} Y_l^l(\theta, \phi) = c_l e^{im\phi} \frac{1}{\sin^m \theta} \left(\frac{\partial}{\partial \cos \theta}\right)^{l-m} \sin^{2l} \theta$$

holds for $m \geq 0$. (at $m=0$, $\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \dots$)

$$\Rightarrow Y_l^m(\theta, \phi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)}{4\pi} \frac{(l+m)!}{(l-m)!}} e^{im\phi} \frac{1}{\sin^m \theta} \left(\frac{\partial}{\partial \cos \theta} \right)^{l-m} \sin^{2l} \theta \quad 43$$

for $m \geq 0$.

Using Rodrigues' formula: $P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l$

$$Y_l^0(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta) = \frac{(-1)^l}{2^l l!} \frac{d^l}{dx^l} (1-x^2)^l$$

That's why we need $(-1)^l$ in C_l .

• One can also start from $m = -l$:

$$Y_l^{-l}(\theta, \phi) = \frac{1}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} e^{-il\phi} \sin^l \theta \quad \parallel \text{No extra phase } (-1)^l \text{ is given!}$$

Applying $\left(\frac{L_+}{\hbar}\right)^{l+m}$, $\parallel m \leq 0$

$$Y_l^m(\theta, \phi) = \frac{(-1)^{l+m}}{2^l l!} \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-m)!}{(l+m)!}} e^{im\phi} \sin^m \theta \left(\frac{\partial}{\partial \cos \theta} \right)^{l+m} \sin^{2l} \theta$$

prove it by yourself!

$$\Rightarrow Y_l^0(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta).$$

and it verifies $Y_l^{-m}(\theta, \phi) = (-1)^m [Y_l^m(\theta, \phi)]^*$.

Summary.

$$\text{Thus, } Y_l^{|m|}(\theta, \phi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)}{4\pi} \frac{(l+|m|)!}{(l-|m|)!}} e^{i|m|\phi} \frac{1}{\sin^{|m|} \theta} \left(\frac{\partial}{\partial \cos \theta} \right)^{l-|m|} \sin^{2l} \theta.$$

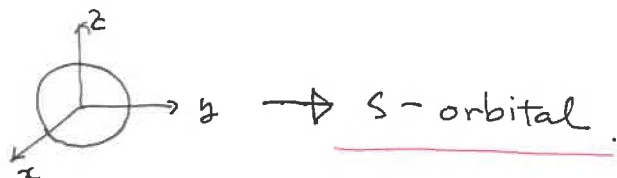
and,

$$Y_l^{-|m|}(\theta, \phi) = (-1)^{|m|} [Y_l^{|m|}(\theta, \phi)]^*.$$

... Spherical Harmonics.

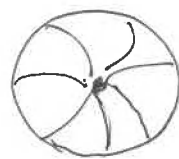
* Plots of $|Y_l^m(\theta, \phi)|^2$

$$Y_0^0(\theta, \phi) = \sqrt{\frac{1}{4\pi}}$$



$$Y_1^{\pm 1}(\theta, \phi) = \mp \sqrt{\frac{3}{8\pi}} e^{\pm i\phi} \sin \theta$$

$$= \mp \sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r}$$



donut

$$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$= \sqrt{\frac{3}{4\pi}} \frac{z}{r}$$



→ p-orbitals

p-orbitals

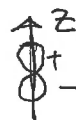
$$P_x \text{-orbital} \Leftarrow \frac{1}{\sqrt{2}} (Y_1^{-1} - Y_1^1) \propto \frac{x}{r}$$



$$P_y \Leftarrow \frac{i}{\sqrt{2}} (Y_1^{-1} + Y_1^1) \propto \frac{y}{r}$$



$$P_z \Leftarrow Y_1^0 \propto \frac{z}{r}$$



$$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}} e^{\pm 2i\phi} \sin^2 \theta = \sqrt{\frac{15}{32\pi}} \frac{x^2 - y^2 \pm ixy}{r^2}$$

One node in $(0, \pi)$

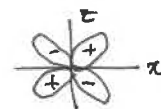
$$Y_2^{\pm 1} = \mp \sqrt{\frac{15}{8\pi}} e^{\pm i\phi} \sin \theta \cos \theta = \mp \sqrt{\frac{15}{8\pi}} \frac{z(x \pm iy)}{r^2}$$

$$Y_2^0 = \sqrt{\frac{15}{16\pi}} (3 \cos^2 \theta - 1) = \sqrt{\frac{15}{16\pi}} \frac{3z^2 - r^2}{r^2}$$

$$d_{z^2} \Leftarrow Y_2^0 \propto \frac{3z^2 - r^2}{r^2}$$



$$d_{xz} \Leftarrow \frac{1}{\sqrt{2}} (Y_2^{-1} - Y_2^1) \propto \frac{xz}{r^2}$$

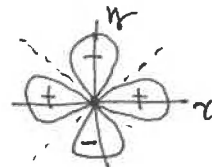


$$d_{yz} \Leftarrow \frac{i}{\sqrt{2}} (Y_2^{-1} + Y_2^1) \propto \frac{yz}{r^2}$$

similar

$$d_{xy} \Leftarrow \frac{i}{\sqrt{2}} (Y_2^{-2} - Y_2^2) \propto \frac{xy}{r^2}$$

$$d_{x^2-y^2} \Leftarrow \frac{1}{\sqrt{2}} (Y_2^{-2} + Y_2^2) \propto \frac{x^2 - y^2}{r^2}$$



Two nodes

"d"-orbitals